



Short communication

Production of diethyl carbonate from ethylene carbonate and ethanol over supported fluoro-perovskite catalysts

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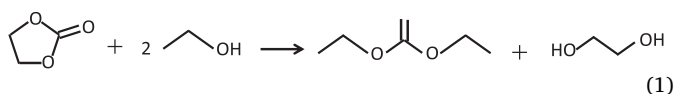
Fluoro-perovskite
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ABSTRACT

The KCaF_3/C (K-Ca(A)) catalyst was shown to be effective as heterogeneous basic catalysts for the transesterification of ethylene carbonate (EC) and ethanol among fluoro-perovskite (XYF_3/C) (X = K, Cs, Y = Mg, Ca) catalysts. Although the KMgF_3/C (K-Mg (A)) catalyst exhibited the highest catalytic activity among the XYF_3/C catalysts studied, the potassium leaching was observed on K-Mg (A). CO_2 temperature programmed desorption (TPD) revealed that the superior catalytic activity of the XYF_3/C was due to its strong basic sites. CO_2 -TPD and XPS measurements indicated that strong basic sites are generated by an increase in the electron density of fluorine.

1. Introduction

Diethyl carbonate (DEC) has been applied as a solvent for paint and fragrances, the electrolyte in Li-ion batteries, and as an ethylation or carbonylation reagent in organic synthesis [1–3]. DEC has also received attention as an oxygen-containing fuel additive [3–5]. The transesterification of ethylene carbonate (EC) and ethanol (Eq. (1)) for the production of DEC is an environmentally harmonized process because the EC reactant is produced through the reaction of ethylene oxide and carbon dioxide, which is a greenhouse gas (Eq. (2)) [2,6].



Basic catalysts are effective for catalyzing the transesterification reaction. Various solid basic catalysts have been reported for this purpose, including alkaline earth metal oxides [7–13], polymer resins [14], and basic zeolites [15], because the separation and recovery of these catalysts is easier than that of conventional homogeneous basic catalysts. Among them, alkaline fluorides are an attractive choice due to their high catalytic activity in transesterification reactions [2,6,12,16,17]. For instance, we recently reported that supported fluoro-perovskite catalysts, which are prepared by an impregnation method, are effective for the transesterification of an edible oil doped with fatty acids and methanol [18].

A mechano-chemical technique has been often used for various complexes synthesis at lower temperature [19–21]. The application to supported catalyst preparation is expected to highly disperse active component. Therefore, the present study was applied the mechano-chemical treatment to the preparation of supported fluoro-perovskite catalysts.

The purpose of the present study was to explore the effects of the alkali and alkali earth metals and catalyst preparation procedure on the catalytic performance of activated carbon-supported fluoro-perovskite (XYF_3/C , X = K, Cs, Y = Mg, Ca) catalysts during the transesterification of EC and ethanol.

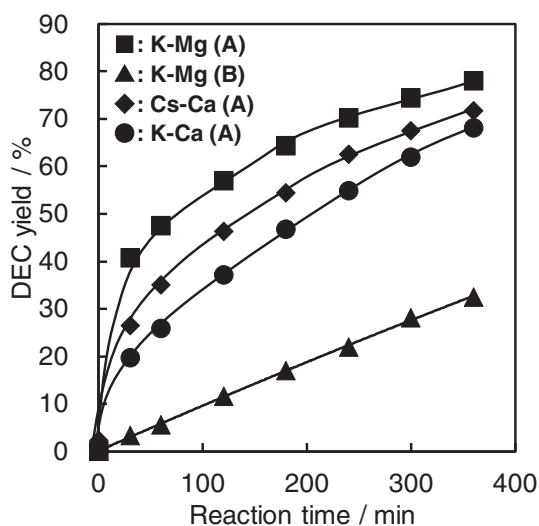
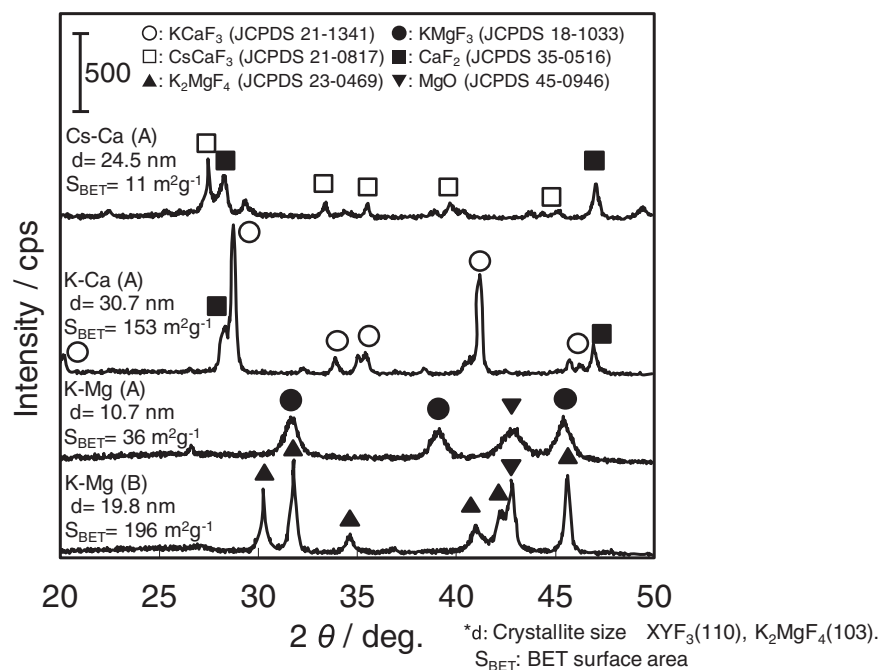
2. Experimental

Supported fluoro-perovskite catalysts were prepared using a mechano-chemical method. Activated carbon (FY-1, Cataler, $S_{\text{BET}} = 800 \text{ m}^2 \text{ g}^{-1}$), SiO_2 (Q-6, Fuji Silysia, $S_{\text{BET}} = 275 \text{ m}^2 \text{ g}^{-1}$), or Al_2O_3 (JRC-ALO-6, a reference catalyst of the Catalysis Society of Japan, $S_{\text{BET}} = 161 \text{ m}^2 \text{ g}^{-1}$) was used as the support. Alkaline fluoride (XF, where X = K, Cs) and alkaline earth hydroxide ($\text{Y}(\text{OH})_2$, where Y = Mg, Ca) were combined with the support powder and zirconia balls in zirconia vessels. In the case of an unsupported KMgF_3 catalyst, KF and $\text{Mg}(\text{OH})_2$ were combined with zirconia balls in zirconia vessels. The molar ratio of the alkaline metal to the alkaline earth metal was 3:1. The molar amount of the alkaline earth metal relative to the support powder was $20 \text{ mmol g}_{\text{support}}^{-1}$. The zirconium vessels were placed in a planetary ball mill (Frisch, P-7), and the mechano-chemical treatment was performed at a rotation rate of 800 rpm for 30 min. As shown in the

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Fig. 1. XRD profiles of as-prepared catalysts.

Fig. 2. Catalytic activities of XYF_3/C catalysts.

XRD profile of K-Mg(A) after the milling process (Fig. S1), the desired fluoro-perovskites were formed during this step according to the following equation,



In order to eliminate the alkaline hydroxide byproduct from the catalyst, the material obtained from the mechano-chemical treatment was washed three times with methanol and then dried at 373 K for 12 h, and finally calcined at 773 K for 1 h in a stream of N_2 (termed catalyst (A)). In addition, the K-Mg catalyst was also prepared with the calcination and washing steps reversed (termed catalyst (B)). The flowcharts for the both preparation procedures were described in supplementary material (Fig. S2).

The transesterification of EC was performed using a batch reactor. The reaction conditions were as follows: 10 mmol of EC, 400 mmol of ethanol, 0.5 g of catalyst ($0.57 \text{ g}_{\text{cat}} \text{ g}_{\text{EC}}^{-1}$ of the amount of catalyst to EC), reaction temperature of 343 K. The amounts of reactants and products were determined using a flame ionization detector/gas

chromatograph (FID-GC; DB-1 capillary column, 60 m, 0.52 mm i.d., GC-14B, Shimadzu). The DEC yield was defined as:

$$\text{DEC yield} = \frac{\text{molar amount of DEC formed}}{\text{molar amount of EC charged}} \quad (4)$$

To examine the reusability of catalyst, 2nd run test was performed. After the 1st run test, the catalyst was separated from the reaction solution by filtration, the separated catalyst was washed with ethanol and then dried at 373 K, calcined at 773 K. the resultant material was used to the 2nd run test.

The Brunauer–Emmett–Teller (BET) surface areas of the newly-prepared catalysts were determined by N_2 adsorption at 77 K using a flow absorption apparatus (Flow sorb II 2300, Micromeritics). The composition of the flow gas was N_2 : He = 30: 70 on a volume basis. Each catalyst was degassed at 473 K for 15 min, prior to measurement. X-ray diffraction (XRD; RINT2000, Rigaku) analysis was performed using Cu $K\alpha$ radiation. The size of fluoride crystallites was calculated using the Scherrer equation. CO_2 temperature programmed desorption (TPD) measurements were carried out with a pulse reactor in conjunction with a mass spectrometer (M-200GA-DM, Canon Anelva) to detect desorbed carbon dioxide at $m/z = 44$. Catalyst samples were pretreated at 773 K for 1 h in a stream of helium. After cooling, carbon dioxide was adsorbed on the catalysts at ambient temperature and CO_2 -TPD data were acquired at a heating rate of 10 K min^{-1} in a stream of helium up to a maximum temperature of 1073 K. X-ray photoelectron spectroscopy (XPS) was performed using a Quantum 2000 (Ulvac Phi) instrument with an Al anode, a beam diameter of 100 μm and an acceleration voltage of 15 kV. Leaching tests for alkaline metal were carried out with an atomic absorption spectrometry (AAS; AA-7000, Shimadzu). Absorption wavelengths for K and Cs were 767 nm and 827 nm, respectively. After the separation of catalyst by the filtration, the alkaline metal concentration in the reaction solution was analyzed.

3. Results and discussion

As shown in Fig. S3, K-Ca(A)/C (Activated carbon) exhibited the highest catalytic activity among the supported K-Ca (A) catalysts. In addition, the catalytic activity of K-Mg (A)/C was higher than that of unsupported K-Mg (A) catalyst (Fig. S4). Hereinafter, the activated carbon was used as the support. As shown in Fig. 1, diffraction peaks

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